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CHEMICAL KINETIC REGIMES OF HYPERSONIC FLIGHT SIMULATION

· By

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TECHNICAL DOCUMENTARY REPORT NO. AEDC-TDR-63-3

January 1963

1963

AFSC Program Area 750A, Project 8952, Task 895208

ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

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ABSTRACT

The requirements for hypersonic test facilities are evaluated on the basis of chemical kinetic phenomena. Flight conditions are divided into three broad chemical kinetic regimes, CHEMICAL EFFECTS NEGLI-GIBLE, NON-EQUILIBRIUM CHEMISTRY, and CHEMISTRY IN EQUI-LIBRIUM. On the basis of this division, it is recommended that a wide class of hypersonic testing, particularly that relating to low density phenomena, be accomplished without full simulation of flight conditions. Approaches to the simulation of flight in the non-equilibrium regime are suggested, and a brief review of the equilibrium regime indicates that test capability may be limited more from economic rather than technical considerations.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.

DCS/Research

Jean A. Jac

Colonel, USAF

DCS/Test

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NOMENCLATURE

 C_p Specific heat at constant pressure Enthalpy h Forward reaction rate coefficient kf Reverse reaction rate coefficient $\mathbf{k_r}$ L Characteristic length M Catalytic collision partner in chemical reactions Pressure р R Specific gas constant R_b Nose radius of body Shock radius of curvature at the stagnation streamline $R_{\mathbf{g}}$ T Temperature, °K Time V Velocity Mass fraction Z Compressibility factor in equation of state Ratio of specific heats γ Δ Shock stand-off distance € Density ratio across shock, ρ_1/ρ_2 Density

SUBSCRIPTS

1	Free-stream conditions
2	Post-shock conditions
equil	Molecular vibration in equilibrium
i	i'th chemical species
O ₂ , N ₂	Molecular oxygen or nitrogen as collision partners in dissociation reaction

1.0 INTRODUCTION

The adequacy of hypersonic test facilities is evaluated on the basis of chemical kinetic phenomena. This study is particularly important if attention is focused on complex manned flight vehicles. Such a goal implies a requirement for extensive research and development in ground test facilities, such as shock tunnels, aeroballistic ranges, perfect gas hypersonic tunnels, and arc- and magnetogasdynamic-driven hypervelocity facilities. A program which exploits the capabilities of each type of facility must be based upon a clear definition of the magnitude of the dominant aerodynamic phenomena. One such phenomenon, considered here from the viewpoint of facility requirements, is the chemical kinetics of air produced by the high temperatures aft of hypersonic shock waves.

On the basis of chemical kinetic phenomena, flight conditions are divided into three areas of importance as follows:

- a. CHEMICAL EFFECTS NEGLIGIBLE Chemical effects may be defined as being negligible under two separate conditions—either the flight velocity and air temperatures about a vehicle are not high enough to produce dissociation or the air density is low to the point that the flow is essentially frozen at the atmospheric composition, i. e., dissociative relaxation lengths are large compared to the size of the vehicle.
- b. NON-EQUILIBRIUM CHEMISTRY In this regime, chemical reactions are calorically important, although the air density is not high enough to produce equilibrium chemistry.
- c. CHEMISTRY IN EQUILIBRIUM At lower altitudes the chemistry is essentially in equilibrium in regions of compressive flow, i. e., in the stagnation region of a blunt-nose body and on the windward side of a body at an angle of attack. Even in this case, portions of the flow may be frozen or in non-equilibrium in the reverse rate (recombination) direction, such as occurs in regions of expansive flow downstream of a blunt nose (Ref. 12). A further division between this case and the case where equilibrium exists throughout the flow field is not attempted.

In all cases, the divisions depend upon the vehicle configuration and orientation. A few characteristic cases will serve to demonstrate the differences.

Manuscript received January 1963.

2.0 CRITERIA FOR CHEMICAL EFFECTS NEGLIGIBLE

A dividing line is established between the regimes of CHEMICAL EFFECTS NEGLIGIBLE and NON-EQUILIBRIUM CHEMISTRY based upon the criterion that no more than 10 percent of the oxygen is dissociated over the flow region of interest. Two different flow regions of interest representing two characteristic flight configurations are considered (Fig. 1). In the first case, the flow is that in the nose region of an axisymmetric body with a nose radius of one foot, and in the second case, the flow behind a 45-deg planar shock is considered as representative of the flow on the windward side of a winged body at an angle of attack.

By considering only the oxygen dissociation reaction in establishing when the chemistry is calorically important, it is implied that all other reactions, notably the dissociation of N2, are energetically of less or at most of equal importance. Inspection of particular solutions for normal shocks (Refs. 5 and 9) and for the blunt-nose region (Ref. 6) in air indicates that when oxygen is 10 percent dissociated the atomic nitrogen is always less than 10 percent of its equilibrium value and, at least for velocities less than 20,000 ft/sec, the nitrogen concentration is always less than the oxygen concentration. The caloric or gasdynamic effect of the other reactions is included in the already somewhat arbitrary definition of the criteria.

2,1 FLOW IN THE NOSE REGION OF A BLUNT BODY

Behind the bow shock, it is assumed that dissociation is zero while the translational and rotational energy of the air are equilibrated. Relaxation of the vibrational energy is roughly accounted for by assuming that vibration is excited to one-half its classical maximum, i. e., vibration of the diatomic species adds one classical degree of freedom to the internal energy of the molecule. This is similar to the simplification made by Lighthill (Ref. 1) for a two-component dissociating gas. Each molecular species, then, behaves calorically like a Lighthill gas, although the reason for the assumption differs from that of Lighthill. In this report the simplification is introduced to account for vibrational relaxation, whereas Lighthill employed it to simplify the analyses of both equilibrium and non-equilibrium flow on the basis that, where the errors in vibrational energy are largest, the errors in the total energy are small because of the overpowering effect of dissociation. It should be emphasized that the vibrational relaxation being considered now applies in a gross way only to gasdynamics. Its effect on dissociation rates is discussed separately in section 2.3.

With the above assumptions, the conditions behind the shock may be calculated for a thermally and calorically perfect gas. The enthalpy of the gas, summing over all i'th species,

$$h = \sum_{i} x_{i} \left[\int C_{p_{i}} dT + h_{o_{i}} \right]$$
 (1)

becomes, simply,

$$h = 4 R T \tag{2}$$

when minor species such as argon, water vapor, etc., and the enthalpy at T = 0, h_{0i} , are neglected.

The gas constant, R, is based upon an air model with mole fractions of 0.21 of O_2 and 0.79 of N_2 , giving a molecular weight of 28.85.

Assuming strong shock conditions, the density ratio across the bow shock is (Ref. 2)

$$\frac{\rho_2}{\rho_1} = \frac{\gamma + 1}{\gamma + 1} \tag{3}$$

where the ratio of specific heats based upon assumed caloric gas properties is

$$\gamma = \frac{4}{3}$$

giving

$$\frac{\rho_2}{\rho_1}$$
 - 7

The following post-shock conditions on the stagnation streamline are then established:

The characteristic dimension for the flow in the nose region of a blunt axisymmetric body is taken to be the shock stand-off distance. From Ref. 3 the approximate constant density solution for the shock stand-off distance, Δ , is

$$\frac{\Lambda}{R_n} = \frac{\epsilon}{1 + \sqrt{\frac{8\epsilon}{3}}} \tag{8}$$

where $\epsilon = \rho_1/\rho_2$ and R_B is the radius of curvature of the shock at the axis. In terms of the nose radius of the body, R_b ,

$$\frac{\Lambda}{R_b} = \frac{\Lambda}{R_a} \left(1 + \frac{\Lambda}{R_a} \right) \tag{9}$$

and for $\epsilon = 1/7$

$$\frac{\Lambda}{R_b} = 0.0961$$
 (10)

The criterion for frozen chemistry in blunt-nose flow is that no more than 10 percent of O2 is dissociated over a length approximately equal to the shock stand-off distance. Employing normal shock solutions, the flow in the neighborhood of the stagnation point where equilibrium will always be attained if viscous effects are neglected is not considered in detail. This is a reasonable approach since viscous and heat transfer effects are quite pronounced at the conditions where chemistry is frozen and the assumption of an inviscid stagnation point is no longer valid (Ref. 4).

2.2 CHEMICAL RATE EQUATIONS

The problem is simplified by considering the oxygen dissociation reaction as an indicator for all reactions occurring behind the bow shock. From Ref. 5, it is seen that the depletion of O2 is dominated by the reaction

$$O_2 + M \stackrel{k_f}{=} O + O + M$$
 (11)

and, for the early times in the reaction which are of interest here, the rate of depletion is nearly constant. Therefore, only the initial reaction rate behind the shock needs to be calculated; this required consideration only of O₂ and N₂ as the collision partner, M.

With parenthesized quantities indicating concentrations in the units of moles per cm³, the depletion rate of O₂ via the dissociative reaction is

$$\frac{d(O_2)}{dt} = -(O_2) \left[k_{f_{O_2}}(O_2) + k_{f_{N_2}}(N_2) \right]$$
 (12)

The forward reaction rate coefficients k_{102} and k_{102} for collision partners O_2 and N_2 , respectively, are calculated in two ways: as recommended by Wray (Ref. 5) based upon the measurement of Camac and Vaughan (Ref. 7) and as employed by Hall (Ref. 6) based upon the measurements of Byron (Ref. 8). These rates, in cm³/mole-sec, are shown on the following page.

Wray 3.2 x
$$10^{19}$$
 T⁻¹ e^{- $\frac{59_{1}380}{T}$} $\frac{k_{f_{N_{2}}}}{2}$ (13)

Hall 3.6 x
$$10^{24}$$
 T^{-3/2} e^{-\frac{59,380}{T}} $\frac{1}{3}$ kf₀, (14)

The criteria for frozen chemistry establishes a depletion rate in terms of moles per original mole of air which produces a reduction of O₂ of 0.021 mole/original mole over a distance of 0.0961 ft. From the rate equation, assuming ρ_2 , V₂, and the chemical reaction rates constant over this distance, the density at altitude in grams/cm³ as a function of velocity in ft/sec which defines the regime CHEMICAL EFFECTS NEGLIGIBLE is, for each of the reaction rate coefficients,

Wray
$$\rho_1 = 4.96 \times 10^{-20} V_1 T e^{\frac{59,380}{T}}$$
 (15)

Hall
$$\rho_1 = 3.58 \times 10^{-22} V_1 T^{\frac{3}{2}} e^{-\frac{59.380}{T}}$$
 (16)

These equations are plotted in Fig. 2, where density altitude corresponds to the 1959 ARDC Model Atmosphere, and are seen to give essentially the same result. Equation (13) is taken to be representative of both Eqs. (13) and (14) for further comparisons which consider the effects of vibrational lag.

2.3 VIBRATION-DISSOCIATION COUPLING

While a previous assumption (Eq. (2)) accounts in a gross way for the effect of vibrational relaxation on the gasdynamic equations, the detailed effect of vibration lag on dissociation rates has yet to be considered. The reaction rate coefficients (Eqs. (13) and (14)) are both based upon shock tube data for which vibration and dissociation are uncoupled, i. e., vibrational excitation equilibrates before any appreciable dissociation. The data of Byron were obtained at temperatures in the range from 2,800 to 5,000°K, whereas those reported by Camac and Vaughan cover the range from 3, 400 to 7, 500°K. Data obtained by Camac and Vaughan at temperatures up to 12,000°K were not reported in Ref. 7 for the stated reason that those data could not be analyzed because of the coupling of vibration and dissociation. The reported data are limited below 8,000°K, the temperature at which vibration and dissociation rates become comparable. For temperatures where vibration-dissociation coupling is expected to be important, a number of studies (Refs. 5, 6, 7, and 9) have employed the correction factor to the dissociation rate

coefficient developed by Hammerling, Teare, and Kivel (Ref. 10) which accounts for non-equilibrium vibration. As given by Camac (Ref. 7) this correction factor immediately behind a translation-rotation shock when all molecules are in the ground state is, for oxygen,

$$\frac{k_{\rm f}}{k_{\rm leguil}} = \frac{1}{40(1 - e^{-2228/T})} \tag{17}$$

where k_{fequil} is the dissociation rate coefficient for vibration in equilibrium.

Equation (17) is plotted in Fig. 3 in which, for convenience, the temperature has been related to velocity according to the approximate Eqs. (5) and (7). Also shown are three calculated points of Wray (Ref. 5) which include the coupling correction of Hammerling et al.; the initial rates of Wray were non-dimensionalized by the vibrational equilibrium rates of Eq. (13). The faired curve indicates that for velocities above about 20,000 ft/sec the initial O2-dissociation rates follow Eq. (17). The result of using this faired curve to correct Eq. (15) for vibration-dissociation coupling is shown in Fig. 4. Also shown in this figure is a curve derived from the data of Schexnayder and Evans (Ref. 11) based on their empirical dissociation rate coefficient for O2-O2 collisions:

$$k_{\rm f} = 7.71 \times 10^{13} \, {\rm e}^{-\frac{37,400}{\rm T}}$$
 (18)

Assuming, as in Eq. (13), that $k_{fN2} = 2/9 k_{fO2}$, the criterion for frozen chemistry based on Eq. (18) is

$$\rho_1 = 2.05 \times 10^{-14} V_1 e^{\frac{37 \cdot 400}{T}}$$
 (19)

No correction for vibration lag has been applied in this case since the rate coefficient has been established for temperatures up to 10,000°K, where, if measurable effects exist, vibration-dissociation coupling is included in the data. On the basis of arguments relating to the resolution time of the equipment and the relative magnitudes of vibration and dissociation relaxation times, Schexnayder disclaims any measurable effects of vibration lag on both his own data and those of Ref. 7. The conflicting conclusions of Refs. 7 and 11 are not discussed further in this report since for the present purposes the results are essentially the same. That is, the criterion for frozen chemistry employing the empirical rate equation of Ref. 11 is not significantly different from that obtained by applying the vibration-dissociating coupling correction to the rate equation of Ref. 7. The latter method is accepted here as giving the more reasonable specification for the frozen chemistry criterion. At the higher velocities, somewhat faster reaction rates would be obtained if the vibration were considered unexcited rather than excited to one-half its classical value. On the other hand, the estimated reaction rates would be somewhat slower if a vibration-rotation coupling were applied to the data of Ref. 11.

Treanor and Marrone (Ref. 19) have extended the treatment of vibration-dissociation coupling to include the reverse effect of dissociation on the rate of vibrational excitation. As dissociation proceeds, the rate of vibrational excitation is depressed because of a drain on the vibrational energy. Further consideration of this mechanism is not required here, since it has no effect on the initial vibration and dissociation rates immediately behind an assumed translation-rotation shock.

The principal source of possible errors in the calculations appears to be the extrapolation of reaction rate data above velocities of about 15,000 ft/sec, with the magnitude at the vibration-dissociation coupling being but one questionable aspect of the extrapolation. Other factors, such as the neglect of electronic excitation and ionization coupling with the cheaptry, appear to be important only above about 33,000 ft/sec (Ref. 5). Finally, known and calculable errors in the estimated criterion for frozen chemistry caused by the simplifications introduced into the gasdynamic equations are on the order of 10,000 ft of altitude, which could change the overall picture very little.

2.4 OTHER CASES - EQUILIBRIUM ASSUMED AND OBLIQUE SHOCK FLOW

For comparison, other conditions for which chemical effects are small may be calculated. First, the condition for which 10 percent of the O_2 in the air is dissociated behind a normal shock, assuming equilibrium flow, may be readily obtained from a Mollier diagram for high temperature air (from Ref. 13, for example) using post-shock conditions for which Z = p/RT = 1.021. This is shown in Fig. 5 which demonstrates the very strong effect of non-equilibrium chemistry at the higher altitudes. Secondly, as representative of a winged hypersonic vehicle, the same criterion of 10 percent of O_2 dissociated is applied to the flow behind a 45-deg planar shock. In this case the length provided for dissociation to occur is taken to be 10 ft. Retaining the assumption of a strong shock which gives $\rho_2/\rho_1 = 7$ and the caloric properties of Eq. (2), the reaction rate coefficient as recommended by Wray gives as the criteria for CHEMICAL EFFECTS NEGLIGIBLE:

$$\rho_1 = 2.386 \times 10^{-21} V_1 T_0 e^{\frac{594389}{T}}$$
 (20)

After applying a vibration-dissociation coupling correction similar to that in Fig. 3, the result is shown in Fig. 5.

2.5 VARIATIONS ATTRIBUTABLE TO SCALE AND ORIENTATION

Since the density may be scaled inversely as the characteristic length, the line for blunt-nose flow in Fig. 5 is approximately 40,000 ft higher for a 10-ft nose radius and 40,000 ft lower for a 0.1-ft nose radius. A similar variation of the line for oblique shock flows results from increasing or decreasing the shock angle by 15 deg, i. e., 40,000 ft higher for a 60-deg shock and 40,000 ft lower for a 30-deg shock. Approximate angles of attack which correspond to the 60-, 45-, and 30-deg shock angles are 46, 37, and 29 deg, respectively.

3.0 CRITERIA FOR CHEMICAL EQUILIBRIUM

The definition of the region in which chemistry is in equilibrium is considerably more dependent upon the flight vehicle configuration and orientation. Where regions of expansive flow downstream of a blunt nose or leading edge are of importance, non-equilibrium in recombination must be considered even though regions of compressive flow are in equilibrium. While such expansive flows are of considerable interest, the major problem areas in the development of complex flight hardware requires more accurate simulation of the regions of compressive flows where heat transfer rates and pressures are severe. Thus, the region of equilibrium chemistry is based upon the same blunt-nose flow and the flow behind a strong oblique shock as used to define the region CHEMICAL EFFECTS NEGLIGIBLE.

The approach to equilibrium behind a shock is governed by net reaction rates which are much slower than those immediately downstream of the shock. For example, the distance for atomic nitrogen to reach 90 percent of its equilibrium value may be as much as three orders of magnitude greater than the distance for 10 percent of the O_2 to dissociate. Employing the criteria for equilibrium that atomic nitrogen reaches 90 percent of its equilibrium value over one-tenth the characteristic length, i. e., $\Delta = 0.096$ ft for blunt nose and L = 10 ft for a strong 45-deg planar shock flow, the equilibrium flight conditions are as shown in Fig. 6. The shaded division is enclosed by intersecting curves for blunt-nose and oblique shock flows which are established from the normal shock solutions of Ref. 9. These solutions provide a ratio of the equilibrium length to the frozen flow length as defined by the criteria and include at the same time appreciable density and velocity changes which could be neglected in the simplified gasdynamic equations for essentially frozen flow.

4.0 DISCUSSION

The purpose of this study is to establish the effect of chemical kinetic phenomena on requirements for ground test facilities. The most obvious conclusion that may be drawn from the chemical kinetic regimes shown in Fig. 6 relates to the area where chemical effects are negligibly small. Here, aerodynamic forces, moments, and heat transfer coefficients may be accurately established employing simulation in terms of Mach number and Reynolds number as well as the appropriate combination of these two in the low density regimes. At the higher altitudes, the energy density required for chemical reactions need not be reproduced since time is not available for any appreciable reaction to occur.

4.1 LOW DENSITY FROZEN FLOW

For the aerodynamic simulation of flight above an altitude of 200,000 ft, viscous and molecular effects are pronounced. The increasing importance of the viscous and molecular properties of the flow is demonstrated in Fig. 7 where the rarefied gas regimes as defined by Probstein (Ref. 14) are compared to the chemical kinetic regimes for a body with a nose radius of one foot. Proceeding downward from altitudes above 400,000 ft where free-molecule flow exists, the flow field develops a shock structure in which the viscous layer is merged with the shock layer. A viscous layer, distinguishable from the shock layer, eventually thins to the point where boundary-layer theory is applicable below about 250,000 ft.

The aerodynamics of flight above 300,000 ft are difficult to simulate in a low density hypersonic wind tunnel because of such problems as nozzle boundary-layer growth. The degree of difficulty is further compounded if one requires that hypervelocity flight conditions be duplicated at these altitudes. The futility of such an attempt is demonstrated in Fig. 8 which compares the degree of dissociation in the atmosphere based upon the 1956 ARDC Model Atmosphere* and U.S.S.R. probe measurements to the frozen degree of dissociation in a wind tunnel test section. The frozen degree of dissociation for the wind tunnel is representative of the results calculated for a nozzle expansion process from reservoir conditions which would produce the correct ambient atmosphere if the flow expanded isentropically (chemistry in equilibrium). At

^{*}As stated in the text of the 1959 ARDC Model Atmosphere (Ref. 17) the earlier 1956 edition probably gives a better representation of composition in the altitude range of interest here.

an altitude of 300,000 ft, the degree of dissociation resulting from the non-equilibrium in the wind tunnel nozzle is at least three times that expected in the atmosphere. Although the correct velocity is not required in a low density tunnel, if need be, the wind tunnel nozzle expansion may be tailored to simulate the desired free-stream degree of dissociation which will then persist throughout the flow field because of the long chemical relaxation times behind the shock.

4.2 NON-EQUILIBRIUM REGIME

The simulation of flight conditions is a considerably more complex problem in the region where chemical reactions are calorically important although not in equilibrium. Scaling laws are applicable to this region as pointed out by Camm, et al. (Ref. 15), for the flow behind a normal shock and as extended by Gibson (Ref. 4) for more generalized flows. The scaling laws are valid where the predominant chemical reactions occur through binary collisions in which case the reaction time is inversely proportional to the gas density. Flow fields are similar, then, if the ratio of the reaction time to particle transit time (proportional to L/V_1) is the same, i. e., for V_1/ρ_1L constant. In the simplest case, the reaction time is made to depend upon ρ_1 alone by requiring that the temperature be constant. This is satisfied approximately if V_1 is constant. Thus, the two conditions $V_1 = constant$ and $\rho_1 L$ = constant define the scaling law and allow model size to be varied. Although this binary collision scaling law is a significant simplification, it provides little immediate help in the correlation of wind tunnel data with the free-flight case since the problem of attaining the desired freestream velocity without excessive dissociation frozen-in still remains to be solved. Some immediate application of the simplified binary scaling law may be expected in shock tunnels and aeroballistic ranges.

Definite possibilities exist for extending our large developmental wind tunnel test capabilities into the non-equilibrium chemistry regime. One promising technique under investigation is the magnetogasdynamic acceleration of air to velocities in excess of 20,000 ft/sec with special attention being paid to minimizing the degree of free-stream dissociation. Another and simpler test technique requiring further study is the use of high pressure arc-heated wind tunnels in conjunction with more complex similarity laws which, for example, remove the restriction of V_1 = constant in the simple binary scaling law.

4.3 EQUILIBRIUM REGIME

In the low altitude flight regime where chemistry is in equilibrium, test requirements relating to ballistic weapons and instrument package

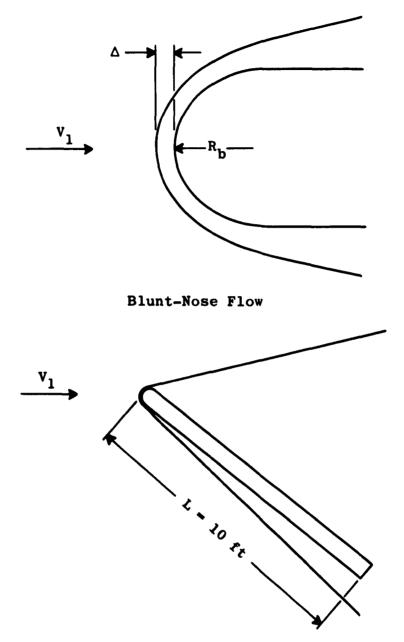
re-entry are rather crude in comparison to the test requirements of the more complex manned vehicles which operate in the non-equilibrium chemistry regime and which are excluded from the lower altitudes because of dynamic force, acceleration, and heat transfer limits. The nature of the tests plus the lessened importance of the degree of dissociation in the flow upstream of the shock relaxes the requirement for the high reservoir pressure needed to duplicate Mach numbers and to suppress the free-stream dissociation. This appreciably reduces the technical obstacle to providing a useful ground test capability in the region where chemistry is in equilibrium. Here, large-scale developmental testing may be precluded more from economic rather than technical considerations.

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Flow Downstream of a 45-deg Planar Shock

Fig. 1 Representative Configurations for Chemical Rate Calculations

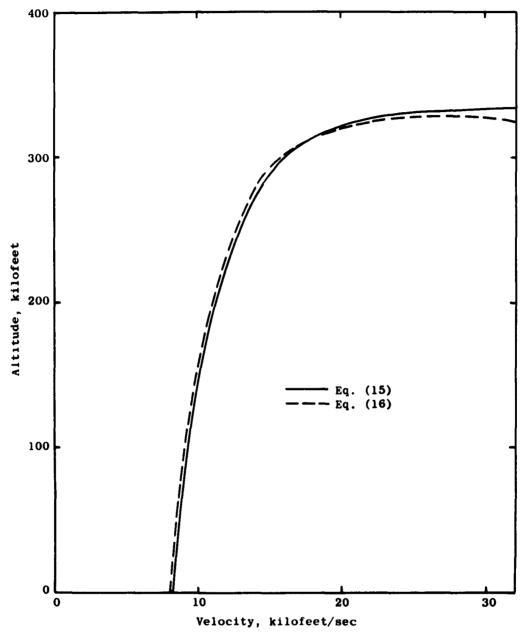


Fig. 2 Flight Conditions above Which Chemistry is Frozen for Blunt-Nose Flow — Vibration and Dissociation Not Coupled

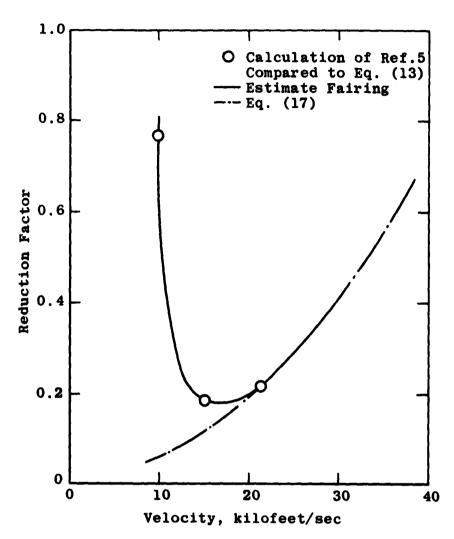


Fig. 3 Reduction Factor in the Initial O₂-Dissociation Rate Caused by Vibrational Lag behind a Normal Shock in Air

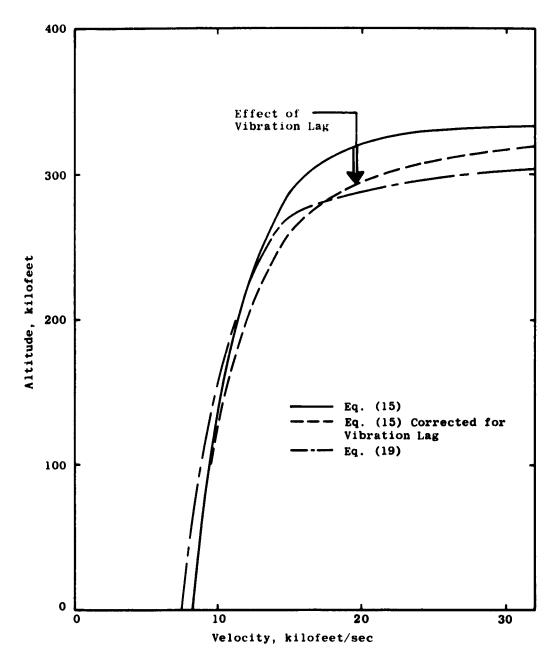


Fig. 4 Flight Conditions above Which Chemistry is Frozen for Blunt-Nose Flow – Including the Effect of Vibration Lag

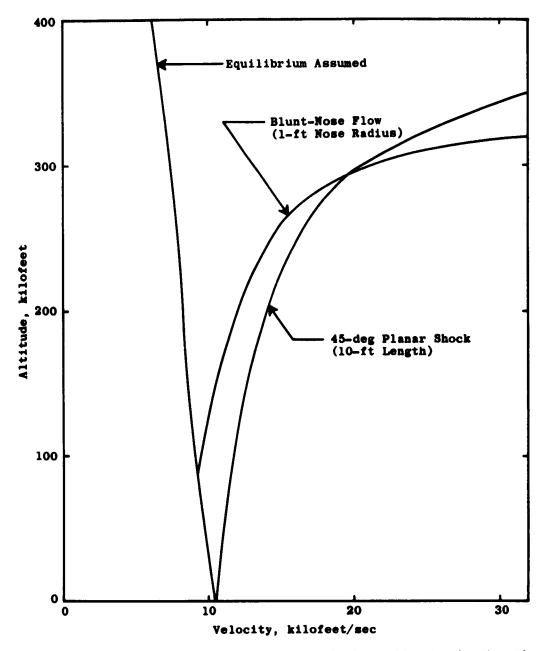


Fig. 5 Criteria for Negligible Chemical Effects Assuming Equilibrium Flow, for Blunt-Nose Flow and for Flow Downstream of a 45-deg Planar Shock

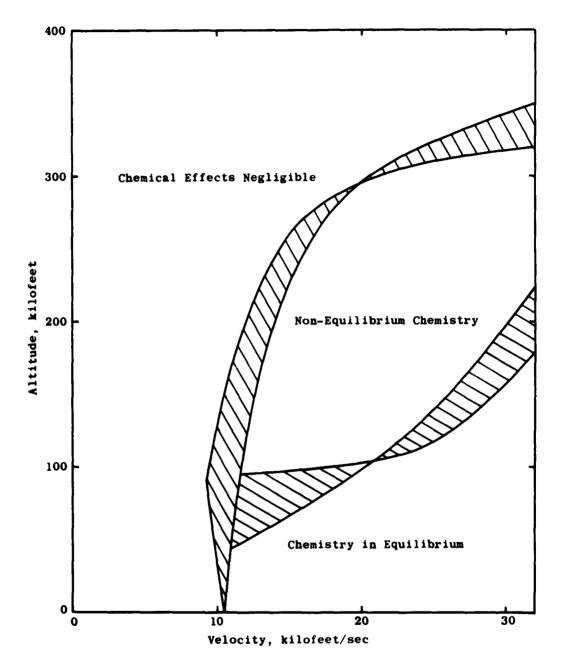


Fig. 6 Chemical Kinetic Regimes of Hypersonic Flight

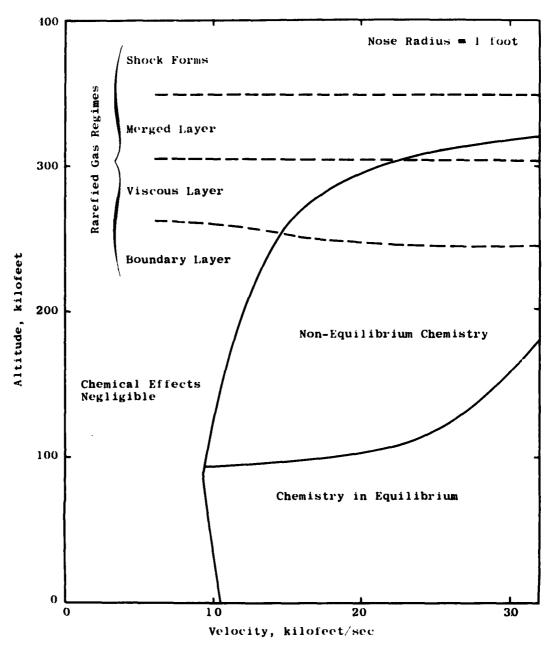


Fig. 7 Comparison of Chemical Kinetic with Rarefied Gas Regimes for Blunt-Nose Flow

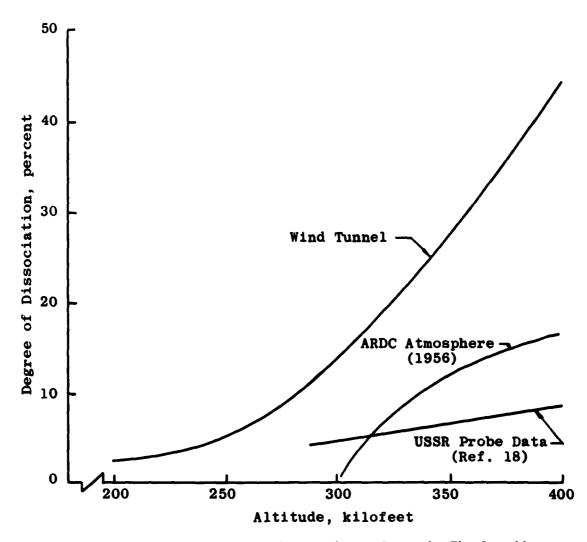


Fig. 8 Percent by Mass Dissociation in the Atmosphere as Compared to That Caused by Non-Equilibrium in a Wind Tunnel Nozzle Expansion Process

1. Hypersonic flight 2. Simulation 3. Dynamics 4. Chemical reactions 5. Chemical equilibrium 6. Blunt bodies 7. Hypersonic wind tunnels 1. AFSC Program Area 750A Project 8952, Task 895208 11. D. J. Harney, Major, USAF 111. Available from OTS 1V. in ASTIA Collection	
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